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Effect of feeding frequency and organic loading rate on biomethane production in the anaerobic digestion of rice straw

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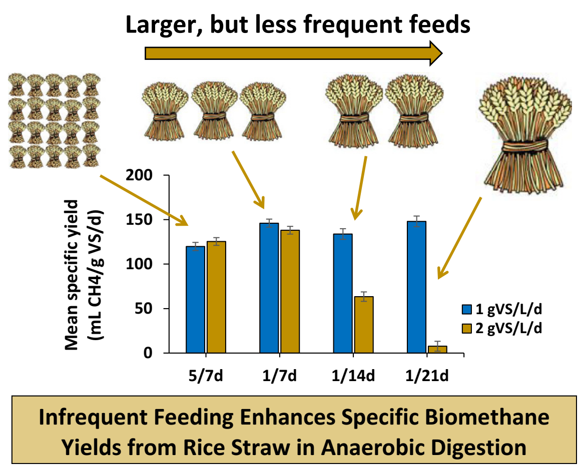
HIGHLIGHTS

- Waste rice straw is abundant and contains massive potential energy.
- Rice straw production is seasonal, therefore AD with infrequent feeding is needed.
- Infrequent feeding (one per 21 days) produced elevated biomethane specific yields.
- VFA accumulation caused AD failure at infrequent feeds at higher OLRs.
- Rice straw AD without pre-treatment or co-digestion is conditionally feasible.

GRAPHICAL ABSTRACT



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ABSTRACT

World energy demand is growing and the negative effects of greenhouse gases (GHGs) and climate change are being felt more acutely. Accordingly, technologies that reduce GHG releases and produce renewable energy, such as anaerobic digestion (AD) with combined heat and power (CHP) systems, are potentially attractive for agricultural wastes, including rice straw (RS). Asia produces over 500 Mt of RS per year that is usually burned, wasting potential energy, causing air pollution and GHGs, and having negative health impacts. Therefore, making RS AD options more attractive is urgently needed. This paper shows biomethane (CH_4) yields from infrequently fed RS AD units, which match better with RS harvest production cycles, can be very efficient at specific CH_4 production without the need for co-digestion. Using Biomethane Potential (BMP) data to guide AD reactor conditions, five feeding frequencies (FFs) were operated for over 250 days in bench-scale units, ranging from five feeds per seven days (5/7; frequent) to one feed per 21 days (1/21; infrequent), using OLRs of 1 g VS/L/d and 2 g VS/L/d. Highest specific methane yields (148 ± 6.3 mL CH_4/g VS/d) were observed at 1/21 FF and the lower OLR. In contrast, highest volumetric yields were seen for a FF of 1/7 at 2 g VS/L/d (276 ± 10.6 mL CH_4/L/d), although AD units failed at this OLR for FFs of 1/14 and 1/21 due to volatile fatty acids accumulation. This study shows RS AD is feasible without co-digestion, producing biogas that can be coupled with CHP technology to provide renewable energy. However, less frequent feeding regimes performed better than more frequent

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feeding regimes, suggesting infrequently-fed batch AD units may be a better option for biomethane production, especially for rural locations.

1. Introduction

World energy demand is forecast to increase by 48% by 2040 and, although this demand will be shared worldwide, increased industrial growth of Asia, particularly China and India, will account for more than half this increase [1]. Further, worldwide greenhouse gas GHG) emissions from agriculture, forestry and fisheries have nearly doubled since the 1960s and could further increase by 30% if no actions are taken [2]. Many areas across Asia also suffer from poor air quality that results in negative health impacts, such as increased stroke, lung disease and chronic pulmonary problems. Therefore, renewable energy options that reduce GHGs and improve health outcomes are needed, including bioenergy production from agricultural waste streams, such as wa ste rice straw (RS).

Approximately 620 Mt of rice was produced worldwide in 2009, equating to around 840 Mt of RS, and production levels are increasing [3]. RS is a fibrous, lignocellulosic biomass with high volatile solids and low bulking density [3,4]; represents around 62% of total crop residues in China; and is the third largest crop residue in the world [5]. RS tends to be produced in large quantities, but irregular cycles (i.e., related to seasonal harvests), which has always posed a problem for using RS as a bioresource. As such, RS is usually left in the fields and-or burnt, resulting in 13,400 t of methane (CH_4) and 800 t of nitrous oxide (N_2O) per year. In fact, Li et al. [6] estimated rice cultivation accounts for up to 5.1 Mt of methane a year, approximately 10% of world emissions.

Although some biofuel crops can be anaerobically digested AD) to release energy, RS has not been widely used despite its massive potential for bioenergy because it historically has been believed to be recalcitrant to AD [3,7]. However, attitudes are changing. The Chinese government is pushing for complete use of RS as a fuel in the near future to combat energy shortages and negative air quality impacts [8]. If RS AD can be made economically feasible, it would address many problems, including air pollution and associated health effects, whilst also reducing a voluminous waste stream and providing a renewable source of methane-rich gas that could couple with combined heat and power CHP) systems. Lim et al. [9] observed that many countries have enough RS resources to generate heat and electricity at the farm or mill-level, and even export surplus power to the grid. Unfortunately, the acyclic production of RS and its reputed poor digestibility still has influenced many against RS AD.

The current 'go to' method to improve RS AD is to use some form of pre-treatment and-or co-digestion, which in some cases has improved biogas yields. However, these options come with costs monetary, technical, or energy); often being impractical at full scale or unworkable within the context of rice farming practice [10-12]. Avoiding pre-treatment and supplements, despite potentially lower yields, has advantages. For example, if it were possible to show that RS AD systems can operate effectively under irregular feeding conditions, AD coupled with CHP becomes more attractive, although suitable RS organic loading rates OLRs must be defined; i.e., feeding frequency FF and OLR must be co-optimised. Would it be optimum to operate with higher, but more intermittent loads for short periods or lower loads spread out over a longer time, and at what OLR? Balancing FF and OLR must be assessed in tandem, although few studies have examined infrequent and-or extreme feeding regimes, such as glut-starve versus steady and regular-fed systems. Most previous work has focused on a narrow time-margins between feeds or tested ranges, such as Bombardiere et al. [13] who examined 1–12 feeds/day for chicken litter waste; Golkowska et al. [14] who tested batch vs semi-batch vs continuous feeding frequencies; Piao et al. [15] twice daily, once daily and bi-daily; and Manser et al. [16], that compared bi-daily vs weekly feeding regimes.

To our knowledge, no studies have assessed a wide range of glut-starve feeding regimes on the biogas productivity and yields in RS AD. Therefore, Biomethane Potential (BMP) assays were first performed to identify "optimal" RS particle size, dairy manure additions to reduce C:N ratios, P additions, and OLRs for subsequent long-term FF experiments. Five different feed-starvation regimes then were assessed in lab-scale AD units to quantify the co-influence of FF and OLR on CH_4 yields and process stability. Two different OLRs were used, creating a two by five matrix of AD operating conditions. Biomethane yields, volatile solids (VS) reduction, and VFA production were monitored to identify optimum feed/OLR options to inform and guide prospective large-scale commercial applications.

2. Materials and methods

2.1. Substrate and inoculum

Rice straw was provided by Professor Yunquan Liu from Xiamen University, China, as uncut lengths of straw that were then ground and homogenized to the desired size, depending upon the experiment. The anaerobic sludge inoculum was a stock solution that had been acclimatised to RS during >100 days in earlier experiments. The RS feed was characterised by its total solids (TS), volatile solids (VS), moisture content (MC), ash content (AC), and fixed solids (FS), total C, N and calorific content, which are summarised in Table 1.

2.2. Biomethane potential (BMP) tests

Preliminary BMP tests were performed according to the VDI 4630 [17] method [18]. Briefly, 300 mL of AD sludge was degassed and combined with 100 mL distilled water, and the appropriate mass of RS in 500 mL flasks (and sealed with a bung). Four factors were assessed in a series of the BMP assays; RS particle size (means, 425 μm, 1.0 mm, 30 mm, 70 mm, and 380 mm – uncut);

Table 1
Characteristics of the rice straw feed and the anaerobic digester inoculum.

Parameter	Unit	Rice straw	Anaerobic inoculum
Total solids	% DW[a]	96.1 ± 0.1[b]	2.4 ± 0.0
Volatile solids	% DW	87.3 ± 0.2	76.6 ± 0.3
Moisture content	% DW	3.76 ± 0.1	97.6 ± 0.0
Ash content	% DW	12.3 ± 0.2	23.3 ± 0.3
Fixed solids	% DW	11.3 ± 2.1	6.18 ± 0.4
C	% DW	39.0 ± 0.4	54.6
N	% DW	0.86 ± 0.1	4.72
C:N	Ratio	45.3	11.6
Calorific content	MJ/Kg	15.4 ± 0.1	–[c]

[a] DW is an abbreviation of dry weight – the weight of sample at standard temperature and pressure.
[b] Standard error (n = 3).
[c] No data for inoculum calorific content.

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C:N ratio (60:1, 50:1, 30:1, 25:1, and 15:1) through addition of dairy manure (DM); P addition with a fixed C:N ratio, using hydrogen phosphate, HPO_4^{-2} (C:N:P = 60:1:0, 60:1:0.1, 60:1:1, 60:1:2.5, and 60:1:5); and OLR (1.0 g VS/L, 1.5 g VS/L, 2.0 g VS/L, 3.0 g VS/L, and 6.0 g VS/L).

BMP assays were performed in series with the particle size assay being performed first using an OLR of 2.0 g VS/L. The first BMP defined the "optimal" particle size for in use the C:N assay, which then defined the optimal C:N ratio for the P addition assay, and optimal C:N:P ratios for the final OLR assay. Blanks containing only AD sludge and water were retained as reference bottles, but provided microcrystalline cellulose in place of RS to create similar physical conditions in the assay vials. All treatment were performed in triplicate at 37 °C and shaken at 100 rpm.

2.3. AD reactor conditions and operations

Five 2.5-L reactors with control towers were used as the AD units, with working volumes of 2.0-L. Each glass airtight-sealed reactor consisted of a heating jacket set to 37 °C, a biogas sampling bag, and a paddle stirrer as shown in Fig. S1 (see Supporting Information; SI). Overall, the reactors were operated for 252 days of which 112 days were used for sludge acclimation to RS feed. During acclimation, the anaerobic sludge inoculum was operated in draw-fill mode (digester sludge removal prior to feed addition) with a 50-day hydraulic retention time (HRT) and an OLR of 1.0 g VS/L/d (chosen based on BMP assays) fed once every seven days. After two HRTs, pH and VFA levels had become stable with time, and the formal experiment was commenced (defined as Time 0). Operationally, OLR1 (defined as "Low") was where 280 mL of reactor volume was removed per week and 14 g VS/week was provided in 280 mL distilled water (as 425 μm RS). For OLR2 (defined as "High"), 28 g VS/wk was provided to the reactors with the same water volume removed as in OLR1.

The first part of the experiment assessed the effect of FF on performance by varying the frequency at which the reactors were fed, including: five feeds every seven days (5/7); three every seven days (3/7); one every seven days (1/7); one every fourteen days (1/14); and day every twenty-one days (1/21). The reactors were operated at OLR1 for 56 days at a mean RS feed rate of 1 g VS/L/d; i.e., some reactors received RS frequently in small amounts, whereas others received less frequent, larger doses. After 56 days, OLR was increased in all reactors to 2 g VS/L/d reactors, which were operated for 84 more days using the same FFs.

Example feed sequences are as follows. For the 5/7 reactor at OLR1, 56 mL of reactor volume was removed per feed and then was provided 56 mL of distilled water, containing 2.8 g VS of RS. This was done five times per week. In contrast, the 1/21 unit had 840 mL removed (per feed) after which 47.7 g RS and 840 mL distilled water were added, but this was only done once every three weeks. The same mean mass of RS was added in both cases, but 5/7 received 15 small feeds in three weeks, whereas 1/21 received one large feed over the same time. Similar withdrawal-feed schedules were used for other FF and OLR reactors, as appropriate.

2.4. CH_4 production and other routine analyses

Gas samples were collected from the assay vials (BMP) or biogas-bag (long-term experiments) using gas tight syringes (SGE and Samco). Samples were collected at the same time of day and analysed immediately to quantify CH_4 content, using a Carlo Erber HRGC 5160 GC-FID fitted with a HP-PLOT Q column at 35 °C with hydrogen as the carrier gas and Atlas software. Specific CH_4 yields (ml CH_4/g VS/d) were calculated daily adjusted for the ambient temperature and pressure.

VFA analysis only was performed in the long-term experiment, typically three or four days per week, depending on the ambient stability of the reactors. Analysis consisted of filtering the sample through a 0.2 μm PES syringe filter before mixing 1:1 with 0.1 M Octane Sulphonic Acid before sonicating for 40 minutes. Samples were then analysed using the Ion Chromatography Dionex Aquion system equipped with an AS-AP auto sampler with Chameleon 7 Software.

2.5. Data analysis and statistics

Statistical analysis of sample data was performed using analysis of variance (ANOVA) with the Tukey comparison and-or *t* tests. Comparisons of mean performance were contrasted among FFs and between OLRs. Significance was defined as 95% confidence in differences (i.e., $p < 0.05$). All statistical analyses were conducted using Minitab 17 (Leadtools Technologies Inc, version 17.1.0, 2014).

3. Results

3.1. Preliminary BMP tests

BMP assays were performed to assess the influence of RS particle size, nutrient ratio, and OLR on specific CH_4 yields to range-find conditions for subsequent longer term FF experiments. Results are summarised in Fig. 1. Relative to particle size, the 425 μm and 1.0 mm cuts had significantly higher yields than 30 mm and 70 mm (Fig. 1a; $p = 0.000$), whereas uncut RS displayed similar yields to the smallest cut (i.e., 183 versus 180 mL CH_4/g VS; $p \geq 0.05$). Due to the small reactors in lab tests here, the 425 μm cut was used for all subsequent tests, although it is noteworthy this particle size produces similar yields to uncut RS, which may be important when extending results to larger scales.

To assess the impact of N addition, DM was added at different C:N ratios and specific CH_4 yields were quantified in the BMP assay (Fig. 1b). In contrast to Yan et al. [19] who suggested 30:1 was optimal, Fig. 1b shows that 60:1, which had no DM addition, had the highest specific CH_4 yield and yields progressively declined with increasing DM addition. Only the 4% DM addition (50:1) yielded a statistically similar amount of CH_4 to no addition ($p \geq 0.05$). Similarly, P additions did not significantly enhance specific CH_4 yields (Fig. 1c). Given a goal was to keep operations simple, DM and P supplements were not provided in the subsequent long-term experiments. Finally, previous work showed OLRs of 1–2 g VS/L were typical for RS [20]. Higher OLRs might be beneficial for reducing reactor size, therefore, OLRs were assessed up to 6 g VS/L in the BMP tests. Fig. 1d shows specific CH_4 yields are similar for OLRs between 1 and 3 g VS/L (i.e., means of 189–175 mL CH_4/g VS), but significantly declined as OLR was increased ($p = 0.000$). Therefore, OLRs of 1–2 g VS/L were retained for the long term tests.

To validate the above tests, experimental methane yields in Fig. 1 were compared with expected theoretical levels based on the elemental make-up of the RS substrate, calculated using previous methods [21-23]. The calculated theoretical yield from RS was 412 mL_{theo} CH_4/g VS, which suggests experimental yields were approximately 45–55% of the maximum and typical of previous experimental studies; e.g. Nielfa et al. [24] (40–50%).

3.2. Effect of feeding frequency on reactor performance

Mean biogas yields, specific and volumetric methane yields, and VS reductions (% VSR) for OLR1 (low loading, 1 g VS/L/d) and OLR2 (high loading, 2 g VS/L/d) are summarised in Table 2 and Fig. 2, which are drawn from time-course data typical of Fig. 3. Time-

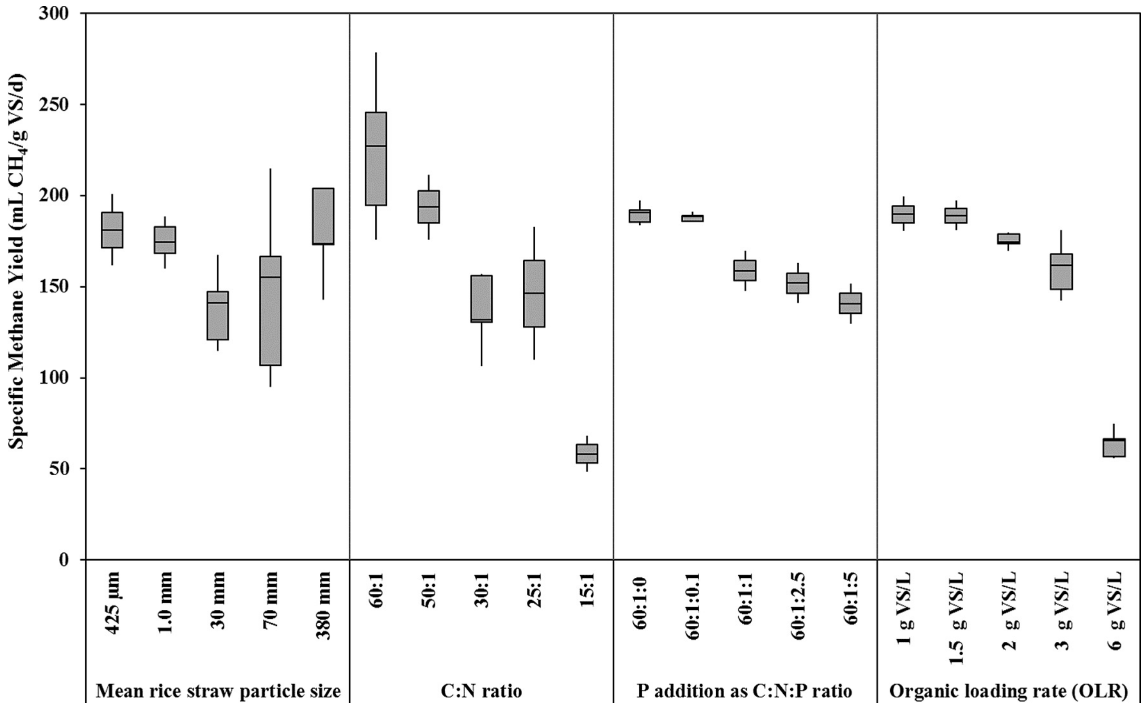

Fig. 1. Mean specific methane yields (mL CH_4/g VS/d) based 30-day BMP tests. Panels include: (a) RS particle size, (b) C:N ratio, (c) P addition with C:N constant, and (d) OLR. Error bars indicate standard errors (n = 3 per treatment).

Table 2
Overall mean performance data for reactors with different feeding regimes and organic loading rates.

Feed Frequency	5/7[a]		3/7		1/7		1/14		1/21	
Organic loading rate (g VS/L/d)	1.0	2.0	1.0	2.0	1.0	2.0	1.0	2.0	1.0	2.0
Biogas (mL/g VS/d)	301 ± 8.4[b]	239 ± 5.1	299 ± 6.8	215 ± 4.6	**317**[c] **± 8.8**	249 ± 5.8	295 ± 9.9	139 ± 10.0	303 ± 11.5	42.0 ± 7.8
% CH_4	40.2 ± 1.3	52.1 ± 1.4	42.4 ± 1.2	52.2 ± 1.7	46.7 ± 1.7	**55.4 ± 1.7**	45.4 ± 1.4	38.7 ± 2.4	49.3 ± 1.4	21.7 ± 1.4
Specific CH_4 (mL CH_4/g VS/d)	112 ± 4.6	125 ± 4.4	127 ± 4.5	112 ± 4.4	146 ± 6.0	138 ± 5.3	134 ± 6.0	63.4[d] ± 5.6	**148 ± 6.3**	7.7 [d] ± 0.7
Volumetric CH_4 (mL CH_4/L/d)	112 ± 4.6	251 ± 8.7	127 ± 4.5	224 ± 8.7	146 ± 6.0	**276 ± 10.6**	134 ± 6.0	127 ± 11.1	148 ± 6.3	15.4 ± 1.3
g VS/L	25.9 ± 0.5	38.3 ± 1.7	25.7 ± 0.6	37.0 ± 1.8	25.4 ± 0.8	41.1 ± 2.0	26.9 ± 1.0	43.8 ± 2.6	27.1 ± 1.2	54.1 ± 3.4
% VS Reduction	**44.1 ± 1.8**	41.6 ± 2.3	42.5 ± 1.9	42.8 ± 1.9	42.5 ± 1.8	40.5 ± 2.2	39.4 ± 2.6	31.7 ± 1.6	38.0 ± 3.2	41.3 ± 3.0
Total VFA (ppm)	147 ± 29.4	432 ± 109	135 ± 18.2	495 ± 163	252 ± 43.7	383 ± 57.8	354 ± 77.2	1730 ± 336	1250 ± 312	3470 ± 355
pH	6.8 ± 0.02	6.7 ± 0.01	6.8 ± 0.02	6.7 ± 0.01	6.8 ± 0.01	6.7 ± 0.01	6.7 ± 0.01	6.3 ± 0.06	6.6 ± 0.02	5.7 ± 0.04

[a] The feeding frequency of each reactor e.g. 5/7 = fed five days out of seven, 1/21 = fed one day out of twenty one. All feeding frequencies have the same net loading of 1g VS/L/d then 2g VS/L/d.
[b] Standard error (For OLR 1.0g VS/L/d n = 56 for biogas and methane, n = 9 for VS; n = 13 for VFA and, n = 30 for pH; For OLR = 2.0g VS/L/d n = 84 for biogas and methane, n = 12 for VS; n = 21 for VFA and, n = 44 for pH).
[c] Bold indicates the highest performing condition for biogas, %CH_4, specific and volumetric methane yields, and % VS reduction.
[d] These reactors failed at the higher OLR of 2 gVS/L/d. 1/14d failed approximately halfway through the experiment and 1/21d failed immediately.

course data for other reactors are presented as Figs. 4 and 5 (discussed later), and Figs. S2 and S3 in the SI. At OLR1, mean biogas yields ranged from 295 ± 9.9 to 317 ± 8.8 mL/g VS/d across the five FF conditions, which did not significantly differ ($p > 0.05$) implying FF did not impact overall biogas production when VS loadings were low. However, specific CH_4 yields (mL CH_4/g VS/d) differed among reactors with the most infrequently fed reactor, 1/21, having significantly higher mean specific yields than the most frequently fed reactor, 5/7 (i.e., 148 ± 6.3 vs 112 ± 4.6 CH_4/g VS/d, respectively; $p = 0.001$). Significant differences between these two FFs also were seen in biogas quality; i.e. 5/7 had a mean CH_4 content of 40.2% ± 1.3 in contrast to 49.3% ± 1.4 for 1/21. Biogas yields, specific CH_4 yields and biogas quality varied among the middle three FFs, but not significantly, although 1/7 tended to have slightly higher yields than 3/7 and 1/14. In contrast to gas results, 5/7 had the highest% VS removal (44.1% ± 1.8) and 1/21 had the lowest (38.0% ± 3.2) (see Table 2), although differences were not significant ($p > 0.05$).

At OLR2, mean biogas volumes ranged from 42.0 ± 7.8 to 249 ± 5.8 mL/g VS/d; however, both 1/14 and 1/21 failed, which explains the wide range (see Figs. 4 and 5). Of the surviving reactors, specific CH_4 yields were significantly different between 3/7 and 1/7 (i.e., 112 ± 4.4 vs 138 ± 5.3 mL/g VS/d, respectively), and there were no significant differences observed in biogas quality (i.e., % CH_4 content).

3.3. Effect of loading rate on reactor performance

Inter-OLR comparison, i.e. 5/7 at OLR1 versus 5/7 at OLR2, etc., showed specific biogas and CH_4 yields always were higher at OLR1. However, significant differences were only seen in inter-OLR specific CH_4 yields for 1/14 and 1/21 ($p = 0.001$), although these were biased by the fact that both 1/14 and 1/21 failed at OLR2. At OLR1, the highest specific CH_4 yield was 1/21 at 148 ± 6.3 mL CH_4/g VS/d, whereas at OLR2, 1/7 had the highest at 138 ± 5.8 mL CH_4/g VS/d; however, these were not significantly different from

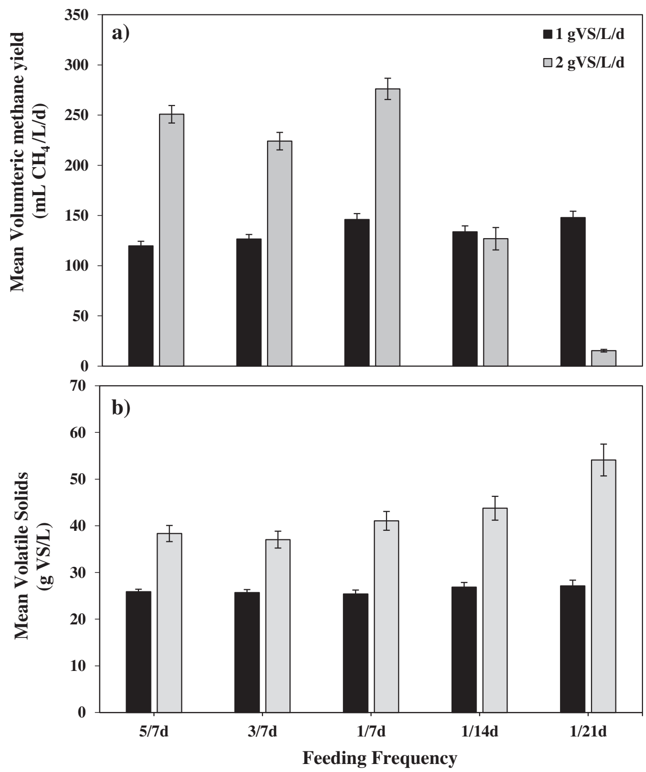

Fig. 2. (a) Mean volumetric methane yield per day for all feeding frequencies and organic loading rates. Standard error bars (n = 56 at OLR 1 g VS/L/d and n = 84 at OLR 2 g VS/L/d). (b) Mean volatile solids for each feeding frequency condition for the whole of each OLR; i.e. experimental mean. Standard error bars (n = 8 at OLR 1 g VS/L/d; n = 13 at OLR 2 g VS/L/d).

each other ($p > 0.05$). Although biogas and specific yields were always higher at the lower OLR, the reactor with the highest CH_4 content in biogas was 1/7 at OLR2 (55.4 ± 1.7% CH_4), significantly higher than 1/21 at OLR1 (49.3 ± 1.4% CH_4; $p = 0.006$).

In contrast to specific biogas and CH_4 yields (where differences were not significant), volumetric biogas (as mL/L/d) and CH_4 (as mL CH_4/L/d) yields were significantly higher at OLR2 ($p = 0.001$). Volumetric CH_4 production at OLR2 ranged from 224 ± 8.7 (3/7) to 276 ± 10.6 (1/7) mL CH_4/L/d compared with 112 ± 4.6 (5/7) to 146 ± 6.0 (1/21) mL CH_4/L/d at OLR1 (see Fig. 2a). In summary, greater CH_4 volumes were produced at OLR2 when the reactor did not fail (i.e., was not overloaded), but more stable operations and higher specific CH_4 yields were seen at OLR1.

3.4. Other indicators of reactor performance

Across all FFs at OLR1, no significant differences were observed in the pH (range 6.6 to 6.8), VS removal (range ~ 38 to 44%), or in VS accumulation (~25.4 to 27.1 g VS/L), although 1/14 had significantly lower VS removal than 5/7 ($p < 0.05$). At OLR2, 1/14 and 1/21 were significantly different for various parameters: i.e., pH (6.3 ± 0.06 and 5.7 ± 0.03, respectively) were significantly lower than for 1/7, 3/7 and 5/7 (all pH 6.7 ± 0.01). VS% removal in 1/14 was significantly lower than the other FFs at OLR2 (32% compared with 40.3 to 44.1%, $p = 0.006$) and VS accumulation was always greater at OLR2 relative to OLR1 (i.e., 37.0 to 54.1 g VS/L vs 25.4 to 27.1 g VS/L, respectively), which may have practical implications to actual RS AD operations.

Time-course data (Figs. 4 and 5) shows that when the OLR was doubled at day 56, declines in performance in 1/14 and 1/21 were almost immediately apparent. For 1/14, Fig. 4 shows VS and VFA became more variable and pH dropped rapidly after feeding,

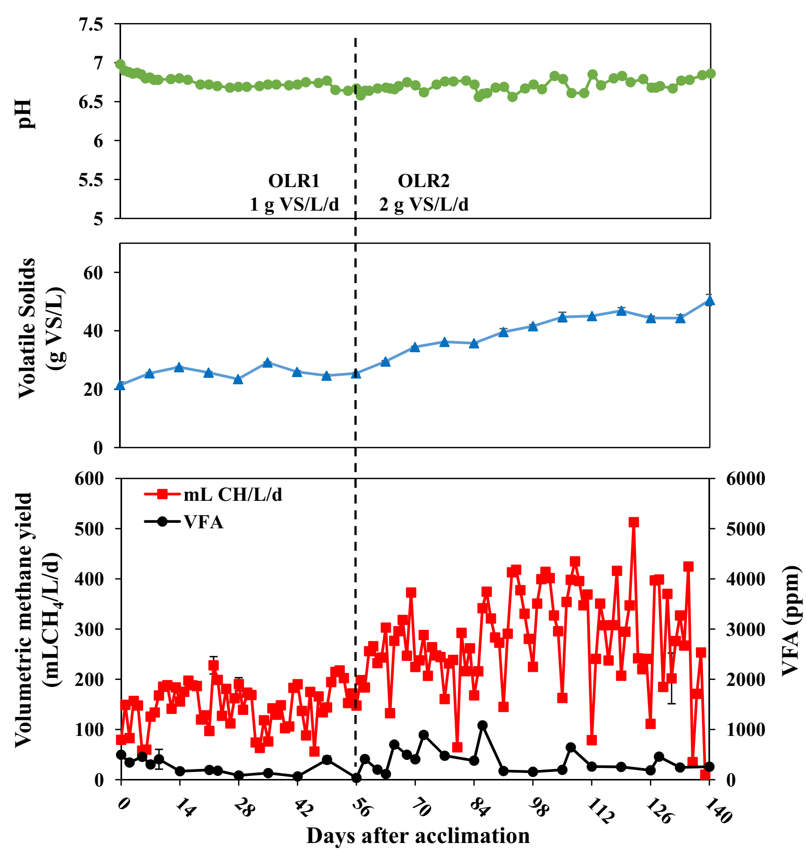

Fig. 3. Time-course performance data for the digester reactor operated with one feed per seven days (1/7). Data are for reactor operations post acclimation, and span OLR1 (1 g VS/L/d) to OLR2 (2 g VS/L/d). pH, volatile solids (g VS/L/d), volumetric methane yields (mL CH_4/L/d), and volatile fatty acid (VFA; ppm) levels are reported over time.

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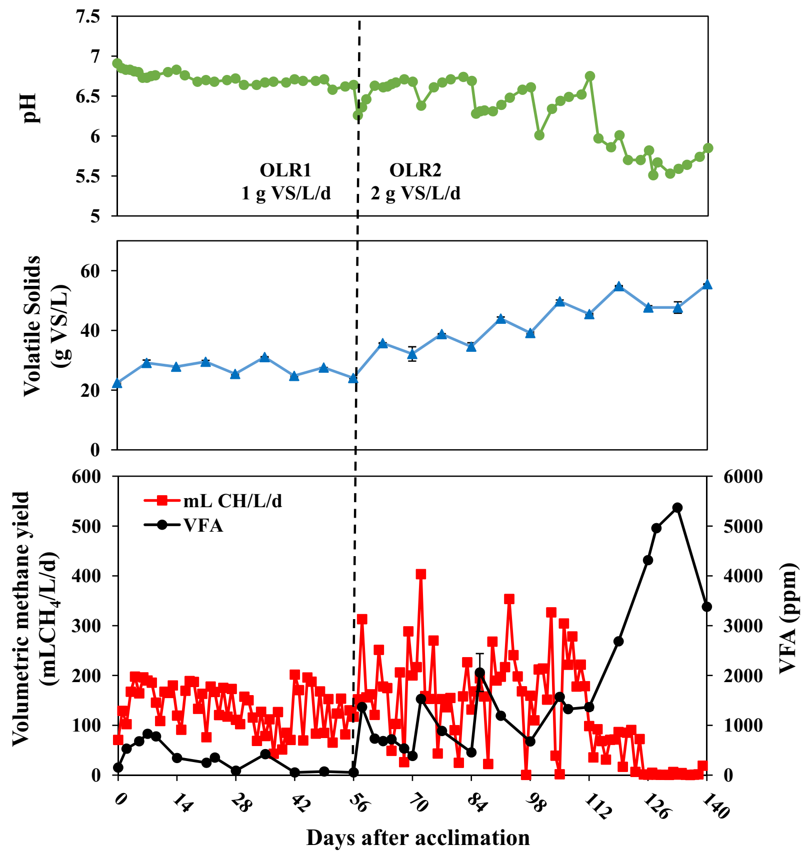

Fig. 4. Time-course performance data for the digester reactor operated with one feed per fourteen days (1/14). Data are for reactor operations post acclimation, and span OLR1 (1 g VS/L/d) to OLR2 (2 g VS/L/d). pH, volatile solids (g VS/L/d), volumetric methane yields (mL CH_4/L/d), and volatile fatty acid (VFA; ppm) levels are reported over time.

ultimately leading to reactor failure on day 112. Whereas, for 1/21, failure occurred almost immediately after the loading change (see Fig. 5). In both cases, mean VFA levels were significantly higher than other OLR2 reactors; i.e., 1730 ± 336 and 3470 ± 355 ppm for 1/14 and 1/21, respectively. Mean VFA levels were significantly higher in 1/21 at OLR2 compared with the other FF units ($p = 0.015$); ~1250 ppm versus <353 ppm in the other reactors.

4. Discussion

4.1. Rice straw AD options

As global energy demand increases, concerns about security, environmental impact, and fluctuating oil prices support the expanded use of renewable energy sources and cleaner technologies [1]. As a result, the energy value of agricultural waste streams has received increased interest, such as the prospect of harnessing energy from RS [25,26]. In fact, China is pushing for complete use of RS as a fuel in the near future [8]. However, the recalcitrance under anaerobic conditions of most straws, due to high lignocellulose content, results in lower CH_4 biogas yield compared with other waste biomass; e.g. RS has only 193–240 L/kg TS compared with rape seed with 300–350 L/kg TS [3,27,28]. This aspect of RS means theoretical yields, such as 330 L CH_4/kg VS calculated by Mussoline et al. [5] or 412 mL CH_4/g VS calculated here, are often much higher than experimental or field values.

Many believe that RS pre-treatment by biological, chemical, or a combination of methods can improve biogas yields [29-31], and some state that lignocellulosic materials must have pre-treatment to ensure degradation [32,33]. Pre-treatment can conditionally help. For example, Chen et al. [34] found that extrusion pre-treatment improved CH_4 yield by 32% compared with milling pre-treatment, Bauer et al. [35] increased CH_4 yields 20% by steam explosion and Zhao et al. [36] increased CH_4 yield by 35% using mild acid pre-treatment. However, Angelidaki and Ahring [37] also found that combining chemical pre-treatment and milling did not increase yields and Gu et al. [38] found inoculum source was a more important factor to yield. Therefore, although pre-treatment is sometimes effective, it comes at a cost monetary, technical, and-or energy), often making full-scale operations impractical or operationally incompatible with actual farming practices [10-12]. Thus, avoiding pre-treatment, despite possibly lower yields, has major advantages.

Methane yields observed in long-term experiments performed here (see Table 2) were higher than Gu et al. [38] who combined RS and granular sludge (~125 mL CH_4/g VS), Lianhua et al. [39] (120 mL CH_4/g VS), and Mussoline et al. [5] (46 mL CH_4/g VS). However, yields were lower than batch experiments by Lei et al. [28] (240 mL CH_4/g VS) and the large scale digesters of Mussoline et al. [40] (181 mL CH_4/g VS). Therefore, our yields are roughly comparable to previous work with variation among studies due to differences in feeding regimes, pH-balancing, scale, and-or pre-treatment. However, results are promising in a practical sense because we show RS AD can operate without major pre-treatment and with less frequent feeding, especially at lower OLRs. Specifically, BMP data here (Fig. 1) show that uncut RS produces roughly the same specific CH_4 yield as heavily cut RS; and manure and-or P addition do not necessarily enhance specific CH_4 yields. In fact, increasing N addition, using DM, was detrimental to RS AD specific CH_4 yields in BMP tests. This is contrary to Estevez et al. [68] but consistent with Contreras et al. [67] who suggested there was no optimum C:N ratio

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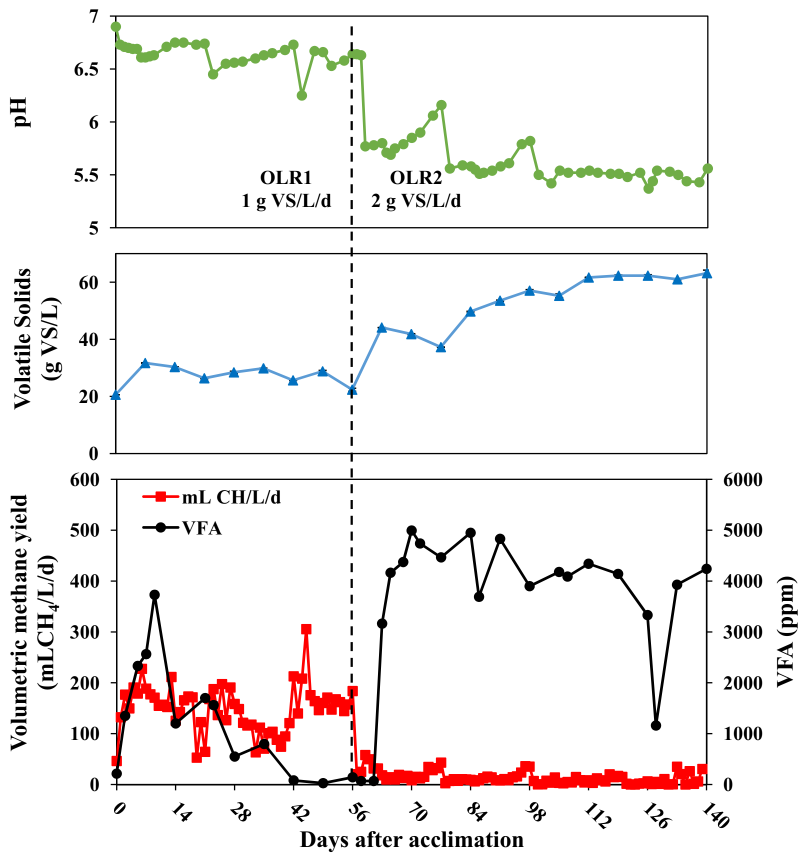

Fig. 5. Time-course performance data for the digester reactor operated with one feed per twenty-one days (1/21). Data are for reactor operations post acclimation, and span OLR1 (1 g VS/L/d) to OLR2 (2 g VS/L/d). pH, volatile solids (g VS/L/d), volumetric methane yields (mL CH_4/L/d), and volatile fatty acid (VFA; ppm) levels are reported over time.

for RS. Similarly, P addition did not alter specific CH_4 yields, which is consistent with Britz et al. [66] for RS AD.

4.2. Biomethane yields and operating options

Rice farms typically have two to three harvests each year, which produce massive amounts of RS over short periods. Given this operating reality, it is surprising few studies have been performed on how irregular RS production patterns influence AD; a bioprocess that usually requires a stable and regular feedstock. Bombardiere et al. [13] did assess the influence of 1–12 RS feeds per day and found more stable operations at less frequent feeding rates. However, their feed frequencies were very short compared with seasonal cycles in rice fields, which work here was designed to assess.

Overall, data show infrequent feeding at low OLRs can provide comparatively higher specific levels of biogas and CH_4 at 1/21 day feed rate (148 mL CH_4/g VS/d), which was higher than the more frequently-fed reactors (see Fig. 2). This is promising for RS AD field applications. However, infrequent feeding at higher OLRs can overload AD systems (Figs. 4 and 5), causing reactor failure. Whereas, higher OLRs with more frequent feeding can produce larger biogas volumes. Therefore, two clear operating options exist for RS AD; less frequent feeding at low OLRs or more frequent feeding at higher OLRs. The preferred option will depend on the space available for RS storage prior to use as well as the quality of the biogas for direct combustion and associated costs, although other considerations exist.

First, the low OLR produced higher specific biogas volumes, whereas the higher OLR produced more volumetric biogas of higher quality in reactors 5/7, 3/7 and 1/7. Doubling the substrate load should, logically, result in increased gross biogas and-or CH_4 yield as seen by Bezerra et al. [41], assuming the AD units are not overloaded, such as 1/14 and 1/21. Although, increasing OLR does not always increase specific biogas yield as seen here and by Babaee and Shayegan [42]. Differences in inter-OLR specific yields in this study were not significant, probably due to the general recalcitrance of RS and greater VFA production during infrequent feeding at OLR2. Nevertheless, volumetric biogas and CH_4 yields were significant between OLRs; OLR2 1/7 (276.1 mL CH_4/L) yielded almost 20% more CH_4 than OLR2 5/7 (224.1 mL CH_4/L at $p = 0.001$), and almost double that of OLR1 1/21 (148 mL CH_4/L at $p = 0.001$).

Second, significantly greater VS accumulation was apparent at the higher OLR. Reactor VS reflects the organic fraction of the substrate that is not degraded by the system [42], and suggest reactors at OLR2 may be receiving more 'substrate' than can actually be degraded. Finally, the more infrequently fed reactors tended to have greater VFA accumulation, especially at OLR2; i.e., 1/21 produced significantly more than all other conditions followed by 1/14. Such acidification can be irreversible and cause a massive drop in CH_4 as seen by Neves et al. [43], or it can be reversible, as indicated by the VFA peaks in 1/7 (Fig. 3), and CH_4 yield can recover as seen by Kawai et al. [44]. However, elevated VFA levels at OLR2 with 1/14 and 1/21 very probably explain failure, which is important to future RS AD practical applications.

As background, rapidly growing, pH-insensitive, acidogenic bacteria tend to overproduce VFAs that the slow growing acetogenic bacteria cannot oxidise [45]. The high VFA values, and large fluctuations in pH, indicate an imbalance between the acid producing bacteria and the CH_4-producing archaea. Excess acid production in AD systems is a common reason for systems to fail or sour as reported by Tait et al. [46] and Franke-Whittle et al. [47], or at least

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negatively affect specific yields [48-50]. There are a number of opinions as to which acids are the best causes-indictors of failure; e.g. Wang et al. [49] and Zhang et al. [51] had low biogas production at 900 and 1000 mg/L of propionic acid, whilst Lianhua et al. [39] and Xu et al. [52] suggested acetic acid was more influential. Both the 1/14 and 1/21 produced average VFA levels of over 1000 ppm, mostly acetic and propionic, with 1/21 having an equal volume of butyric acid. This indicates that the microbial community had reached substrate saturation point and could not progress through complete methanogenesis. However, this might be avoided in prospective applications by identifying microbial 'tipping points' through growth rate analysis and removing a proportion of solids before the system became unproductive.

4.3. Energy implications

The potential for RS AD was assessed to provide sufficient biogas and electrical power for a rural community where the average household requires 4 kW h/d [53]. As background, the average rice farm in Asia is one hectare, producing approximately 7.5 tonnes of RS per hectare per year [54,55]. Therefore, if one scaled-up feed rate from 1.0 g VS/L/d to 1.0 t VS/1000 m^3/d, one would require RS crop from 50 hectares to produce 1.0 tonne of RS per day.

Using data from Table 1 and that of the Munder et al. [56] and RKB [57], the average energy content of RS is 15.5 MJ/kg. Converting MJ/kg into kW h at a 3.6:1 ratio provided by Cuéllar and Webber [58], means that 1 tonne of RS has the potential energy of 4300 kW h. Therefore, using 1 tonne RS per day in an AD unit of 1000 m^3 volume, and CH_4 yields from the OLR1 and also from Mussoline et al. [3] and Wu et al. [59], RS AD/CHP could potentially generate between 400 and 500 kW h/d (assuming 1 m^3 CH_4 equates to an energy content of 36 MJ and an electrical generating efficiency of 35% for the CHP system). However, 800 to 1000 kW h/d electricity could be produced by RS AD/CHP at OLR2, assuming low FFs. If this energy were wholly recovered from the RS AD process, energy yields are similar to average values reported by Mussoline et al. [40] (i.e., 1100 kW/d), and could provide electrical power to 1000 rural households. Conversely, smaller versions of this theoretical system, such as 100 m^3 capacity, may be suitable stepping stones in scaling up the system. This size falls within the range of most small-scale digesters in China, where there are over 30 million AD plants sized 1–150 m^3 [60]. If the potential energy within RS could be released through AD then 100 rural homes would benefit from our method.

Feasibility depends on the costs and impact of RS storage, RS production frequency, the economics of the electricity generation, and the usefulness of heat produced from the CHP system. In a full-scale system, some electrical power and heat would be used on-site to maintain the digester, as well as providing additional electrical power and heat for local community use. For example, heat can be used locally for crop drying whilst the electricity could be sold or used elsewhere. CHP systems can reach up to 90% fuel conversion efficiency and could reduce CO_2 emissions from biofuel generation by as much as 10% by 2030 whilst providing real savings now by reducing the reliance on more expensive power generation [61].

As an added benefit, using anaerobic digestate as a fertiliser has been shown by Nguyen and Fricke [62] to be effective as N, P and trace metal supplements for soils [63]. This "fertiliser" is organic and aids local farmers in reducing their cultivation costs, simultaneously mitigating other environmental impacts and increasing self-sufficiency and financial security [64]. This was shown as feasible by Luo et al. [65], who reported small-scale digesters (operated by trained farmers) can produce usable biogas for a local community with digestate being used to improve rice yields by ~15%.

Finally, as the use of waste biomass-derived gases become more economically viable, they will become increasingly important source of useable energy and play an important role in the reduction of GHGs [61]. AD is not a new process, but the way in which it is harnessed may prove important for remediating these global issues and reaching these energy goals. RS AD will not produce as much as gas as other wastes (per biomass), but due to its massive abundance, it could provide local, national and international benefit if used optimally. However, the scale up of AD is not linear and, as such, any data extrapolated to a larger scale would first require modelling and pilot scale testing.

5. Conclusions

RS is abundant and has high carbon content, but its potential as a renewable energy source has been underutilised due to its perceived poor biodegradability and infrequent production cycles. Therefore, BMP tests on were performed on Chinese RS to assess degradability and supplementation needs for AD. However, it was generally found that N and P additions did not enhance specific CH_4 yields and would only complicate operations. Long-term, CSTR-scale AD experiments then were performed to assess the impact of FF and OLR on specific CH_4 yields and biogas volumes. Highest specific CH_4 yields were seen in least frequently fed AD unit at a lower OLR (i.e., 1/21 at 1 g VS/L/d). In contrast, highest volumetric yields were observed with moderately frequent feeding at a higher OLR (i.e., 1/7 at 2 g VS/L/d). Although both operating options have benefits, low loading with less frequent feeding is probably be better in tune with acyclic waste RS production cycles and may be a better option than current practice. In fact, with sufficient storage, infrequently-fed RS AD with CHP has the potential to generate large quantities of renewable heat and electrical power via a simple process, providing other benefits, such as reduced air pollution, limited pre-treatment and no co-digestion, and improved environmental quality.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.apenergy.2017.05.170.

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